Appendix 5

Supplementary Material for Chapter 5

Part H
Summary of PM Sampler Comparison Study at the Bakersfield Monitoring Station

The purpose of this study was to compare the performance of PM2.5 and PM10 continuous measurement methods to reference methods. Our intent was to identify PM2.5 and PM10 continuous analyzer(s) that can be used to determine compliance with the State ambient air quality standards (AAQS).

In response to a request by the Air Resources Board (a Board), the Office of Environmental Health and Hazard Assessment (OEHHA) and the ARB staff are reviewing the State PM standard. OEHHA has recommended retaining the current PM10 standard, revising the 24-hr and annual average values, and has proposed PM2.5 24-hr and annual standards. As a part of the PM standard review, ARB must describe the method by which particles will be measured and used to determine compliance with the AAQS. That activity resulted in staff reviewing the current PM10 State method (Method P), and identifying methods to measure PM2.5.

In the Board draft staff report, prepared for the Air Quality Advisory Committee, dated November 26, 2001, staff recommended the State adopt the PM10 and the PM2.5 Federal reference method (FRM) samplers that employ inertial impactors as methods suitable for determining compliance with the State standard. Staff also recommended the use of continuous PM10 and PM2.5 analyzers, if possible, that were being evaluated in Bakersfield, CA. Additional testing was necessary to capture the atmospheric conditions in the two areas with the most persistent particulate problems in California, the San Joaquin Valley and the South Coast Air Basin. The testing in Bakersfield adequately represents the conditions in both areas. Moreover, findings for this report needed to be based on a well-controlled study that eliminated vendor involvement, and that used an existing station with agency monitoring staff to operate the equipment. Other rigorous elements incorporated into the study included duplicate instrumentation for all instruments, extensive sample collection, multiple reference samplers, and audits by an outside entity of the candidate and reference devices.

Objectives

The study was conducted to compare the performance of advanced, commercially available continuous PM10 and PM2.5 analyzers to the performance of federal reference methods. These reference methods included duplicate hi-volume SSI and low-volume Partisol samplers for PM10, and the lo-volume RAAS for PM2.5. The resulting data were used to:

1) Determine whether any specific continuous monitoring method(s) is (are) acceptable for measuring PM10 and PM2.5 in California for the State Ambient Air Quality Standard.

2) Compare the common attributes of a lo-vol and hi-vol PM10. This objective was selected to evaluate the effect of using a hi-vol versus the lo-vol sampler as the ‘subtractant’ if one needed to calculate course mass (PM10-PM2.5).

Location of the Study

The study was conducted at the Air Resources Board monitoring station at 5558 California Avenue in Bakersfield, California. Located at the southern end of the Central Valley, the station is situated in a basin created by surrounding mountain ranges. Major activities in the region include oil productions, agricultural operations, and motor vehicle traffic. Bakersfield contains major roadways connecting Northern and Southern California.

Historical air quality data at Bakersfield shows that the winter season in the area sees high levels of air pollution due to emissions, topography, and meteorological conditions. Historically, during the winter months, this region is dominated by high PM concentrations. A large component of this PM consists of volatile compounds (nitrates and moisture).

Conducting the study in fall and winter in this location provided a wide range of meteorological and air quality conditions under which to test the instruments.

Instruments evaluated

Three types of PM10 and four types of PM2.5 continuous samplers were evaluated. Two of each type and size cut were operated for a total of 14 samplers.

The data from the continuous PM10 samplers were compared to two types of reference method, one hi-vol and one lo-vol. The PM2.5 continuous data were compared to the PM2.5 lo-vol reference method.

Reference method samplers

PM10
The Partisol model 2000 (Rupprecht and Patashnick [R&P] Partisol 2000; lo-vol) and the SSI model SA1200 (Thermo Andersen Inc; hi-vol) were the Federal Reference Method (FRM) samplers against which the PM10 continuous samplers were compared. A pair of Partisol PM10 FRMs were provided by R&P for the period of the study. The SSI was also operated in tandem at the site. It is currently the State method for PM10. These samplers are permanently placed at many stations by the ARB and local air districts. The mass of the PM in either instance is determined by pre- and post-weighing the sample filter. The mass concentration of PM is determined by dividing the collected mass by the total amount of air sampled.

PM2.5
The reference ambient air sampler (RAAS 2.5-300, Thermo Andersen Instruments), an FRM for PM2.5, was used to evaluate the accuracy of the

continuous PM2.5 samplers. This sampler consists of a PM10 inlet and a Wells Impactor Ninety-Six (WINS impactor), followed by a Teflon filter. The RAAS operates at 16.7 lpm. The WINS impactor is used to eliminate particles between PM10 and PM2.5 before they are collected on a 47-mm Teflon filter. The concentration of the PM is determined in the same manner as PM10, however using criteria contained in federal regulations specific to PM2.5.

Both lo-vol PM10 and PM2.5 FRMs used louvered PM10 inlets.

Continuous samplers

Four types of continuous samplers were evaluated in the study. All were lo-volume (16.67 lpm). Four samplers were provided by each vendor, two were configured to sample PM10, and two to sampler PM2.5. The participating samplers were the Thermo Andersen Beta Attenuation Monitor (BAM, model FH 62 C-14, here after called And-BAM), the Met One BAM (model 1020, here after called Met-BAM), and the Rupprecht and Patashnick (R&P) Filter Dynamics Measurement Systems (R&P FDMS series 8500). Also two PM2.5 Continuous Ambient Mass Monitor (CAMM) were provided by Thermo Andersen. Each PM10 device was equipped with louvered PM10 inlets and an inertial impactor. The instrument manufacturers assumed the responsibility for installing and calibrating their samplers. ARB staff provided space to the vendors at the air monitoring station. The representatives trained ARB staff and departed the site after they were confident the sampler was performing properly and the staff were suitably trained. The manufacturers' representatives handed over all aspects of the operation of the samplers to ARB staff for the duration of the study.

The PM2.5 samplers were equipped with a PM2.5 sharp cut cyclone (scc) to separate the PM2.5 fraction from the PM10. The cyclone is well suited for continuous operation

Beta Attenuation Monitors (BAM)

A beta attenuation monitor (BAM) consists of a lo-vol size selective inlet, a filter tape, a beta source, a beta ray detector, a lo-vol flow controller, and a timer. The sampler uses a source of beta radiation (^{14}C) and a detector to measure the beta absorption from PM accumulated on the filter tape. The filter material is a roll or cassette that advances automatically on a timed sequence. When particles are placed between the beta source and the detector, the beta rays are attenuated or absorbed by particles in their path. The difference in attenuation before and after the segment of the tape used to collect PM is attributed to the PM deposited on the filter. The reduction in beta ray intensity passing through the collected PM is a function of the mass of material between the source and the detector. The degree of beta radiation attenuation is converted to a PM concentration.

Thermo Andersen BAM (Model FH 62 C14)

The Thermo Andersen BAM (And-BAM) was equipped with an optional intermittent tube heater to reduce the relative humidity so that moisture does not condense on the filter. It performs simultaneous mass collection and measurement with continuous display of the current concentration. The single spot remains in the chamber for particle collection and measurement for 24-hr or until it is full (typ1500 $\mu g/m^3$), although the sampler has the ability of advancing the tape at a preset time. Calibration is accomplished with two calibration foils. It performs auto-zero check and is equipped with temperature sensor. It can measure PM mass as high as 5000 $\mu g/m^3$

Met One BAM (Model 1020)

The Met One BAM (Met-BAM) was also configured to eliminate water vapor from condensing on the filter. It automatically warmed the incoming air to 3°C above ambient. It has a sample time of 50 minutes per hour. The first and last five minutes of the sampling hour are used to calibrate, measure, and calculate the concentration of PM. The tape is automatically moved every hour. The sampler performs auto- zero/span check and is equipped with pressure and temperature sensors. It can measure PM mass as high as 1,000 mg/m^3.

Continuous Ambient Mass Monitor

The continuous ambient mass monitor (CAMM) based on a measure of pressure drop increase across a membrane filter with increasing particle loading on the filter. The analyzer consists of a diffusion dryer to remove particle-bound water and a filter tape to collect PM.

Filter Dynamics Measurement System (Series 8500)

The series 8500 Filter Dynamics Measurement System (FDMS) manufactured by R&P consists of an inlet, a sample filter, a dryer (sample equilibration system or SES), a microbalance, a purge filter conditioning unit, and a control unit. It uses a tapered oscillating microbalance that operates at 30^{o}C to measure the PM mass. It measures the PM mass and corrects for the volatile PM due to the elevated sampler temperature (30^{o}C), and reports the sum of non-volatile and non-volatile PM mass.

Study Period and Sampling Frequency

The study began on October 15, 2001, and ended January 31, 2002. During this period, the PM10 (SSI and Partisol) samplers and one of the PM2.5 (RAAS) filter-based samplers were operated one-in-three day schedule. The second RAAS was operated every day. All continuous analyzers were operated 24 hours a day, 7 days a week.

Data completeness

Data completeness (DC) is a measure of the number of available useable data to the total number of data possible for a single pollutant for a single site. Mathematically it is defined as:

%DC =

$$\left[\frac{total\ number\ samples\ possible - samples\ lost\ due\ to\ calibration\ and\ downtime}{total\ number\ of\ samples} \right] x100$$

For continuous data , there should be at least 18 or more hourly data of the maximum 24 and no more than 2 hours of consecutive hours data missing. The ARB strives for at least 85% DC. Data completeness was determined for both samplers not each one.

Using the above formula, the And-BAM PM10 and PM2.5 provided 86% and 96% DC (Table 1) respectively. The 4% incompleteness rate for PM2.5 was attributed to a wet filter due to roof leak at the sampler tube inlet. The collocated PM10 And-BAM sampler failed an audit on January 29, 2002. Because of this the data generated in January were discarded resulting in 86% DC. The CAMM had 96% DC, most of the 4% incompleteness was attributed to operator error.

The Met-BAM PM10 and PM2.5 samplers provided 90% and 97% DC respectively. Most of the data loss was because of pump problem and the samplers ran out of filter tapes during the weekend.

The FDMS PM10 and PM2.5 provided 92% and 87% DC respectively. The lower %DC of the PM2.5 FDMS (87%) and of the PM10 (92%) were attributed to either the clogging of the sample equilibration systems (dryers) or to the non-zero status provide by the samplers status output. Each of the FDMS samplers had had its dryer replaced once, the instrument provides an hourly status report (non-zero status code) whether the corresponding data is useable or not. Per manufacturer's protocol, the data were considered valid only when the status values are zero. In addition to dryer replacement, data were invalidated due to non-zero status codes.

All samplers achieved the ARB goal for data completeness.

Table 1. Data completeness for samplers used at the Bakersfield sampler comparison study, 10/15/01 to 01/31/02

Samplers	hrs lost to cal	hrs lost to down time[1]	%DC
Thermo Andersen BAM-PM10	4	744	86
Thermo Andersen BAM-PM2.5	4	216	96
Thermo Andersen CAMM PM2.5	4	216	96
Met One BAM-PM10	5	144	90
Met One BAM-PM2.5	13	144	97
FDMS PM10	4	408	92
FDMS PM2.5	11	648	87

[1]includes instrument malfunction, environmental factors (e.g roof leak), operator error, and others

Methods of Data Analysis

To compare the performance of continuous samplers with the FRMs, first 24-hr averages were calculated for each continuous sampler. Then the average of the collocated samplers was compared with the average of the collocated FRMs. When one of the collocated continuous samplers did not produce enough data to produce 24-hr average, the 24-hr average of a single sampler was used for comparison. For precision, daily averages of collocated samplers were compared.

Precision of the FRMs was determined using the equations described in 40CFR Part 58 (Federal Register, 1997). The equations are given below. First the percent difference of each pair of 24-hr average data was calculated using equation 1.

Equation 1

$$di = \left(\frac{sampler1 - sampler2}{Average\ of\ \ (sampler1\ and\ \ sampler2)} \right) X\ 100$$

For a given sampler j, the average of the individual percentage difference during the study can be calculated using.

Equation 2

$$D_{j,q} = \frac{1}{n_{j,q}}\ x \sum_{i=1}^{n_{j,q}} d'_i$$

Where $n_{j,q}$ the number of sample pairs measured during the study. Also, regression analysis of collocated samplers was determined to evaluate the extent of agreement of the two.

To assess the accuracy of the continuous samplers, the averages of continuous PM10 samplers' data were compared with the averages of PM10 Partisol and SSI FRMs. Because of the similarity of flow rate and filter size, the daily averages of the PM10 continuous samplers were compared with the averages of Partisol sampler for accuracy. The averages of continuous PM2.5 samplers' data were compared with the averages of PM2.5 RAAS FRM. A regression analysis of the FRM to each continuous sampler was used to determine a slope, intercept, and correlation.

PM10 sampler comparison

Results of comparisons of PM10 samplers are given in Table 2. The FRMs are the lo-vol Partisol and the hi-vol SSI. Each was evaluated for precision using collocated samplers. The average of collocated Partisol was used to compare with average of collocated continuous samplers for accuracy.

Table 2. PM10 samplers comparison

X	Y	Intercept (ug/m3)	slope	r[1]	# samples
Precision					
Partisol[2]	Partisol	0.26	0.99	1.0	32
SSI[2]	SSI	0.18	1.01	1.0	32
And-BAM[3]	And-BAM	0.86	1.0	0.98	108
Met-BAM[4]	Met BAM	-1.63	0.97	1.0	97
FDMS[5]	FDMS	17.14	1.04	0.93	91
Accuracy					
Partisol	SSI	2.57	0.96	1.0	32
Partisol	And-BAM	-2.50	1.04	0.99	34
Partisol	Met BAM	-1.65	1.13	1.0	32
Partisol	FDMS	1.08	1.05	0.97	30

[1]r = correlation
[2]Partisol and SSI (size selective inlet) are Federal Reference Methods for PM10 manufactured by Rupprecht and Patashnick Co., Inc. and Thermo Andersen respectively
[3]And- BAM = Thermo Andersen BAM model FH 62 C14 manufactured by Thermo Andersen, Inc.
[4]Met BAM = Met One BAM model 1020 manufactured by Met One Instruments, Inc.
[5]FDMS = Filter Dynamics Measurement Systems series 8500 manufactured by Rupprecht and Patashnick Co.,

FRMs

The precision of the samplers, two Partisols (slope = 0.99, correlation 1.0, and intercept 0.26) and the two SSIs (slope = 1.01, correlation 1.0, and intercept 0.18) was excellent. Calculating the precision of each sampler type using equations 1 and 2 above, the Partisol and SSI have precision values of 0.7% and 1% respectively (Table 3).

The agreement of the lo-vol Partisol with the high-vol SSI also shows excellent agreement (r = 1.0) with the slope and intercept of 0.96 and 2.57 respectively. Continuous samplers

Regression analysis of the collocated continuous And-BAM (slope 1.0, intercept 0.86, and correlation 0.98), Met-BAM (slope 0.97, intercept -1.63, and correlation 1.0), and the FDMS (slope 1.04, intercept 17.14, and correlation 0.93) yielded good agreement between pairs.

Table 3. Daily precision for both PM2.5 and PM10 samplers.

	------------Precision (%)-------------	
	PM10	PM2.5
SSI	1	_
Partisol	0.7	_
RAAS	_	4

Comparison of the Partisol to the And-BAM, Met-BAM, and the FDMS resulted in slope values of (1.04, 1.13, and 1.05 respectively), correlation values (0.99, 1.0, and 0.97, respectively), and intercepts (-2.50, -1.65, and 1.08, respectively) which indicate agreement between the continuous sampler and the FRM within the criteria for a California Approved Sampler. (Table 2). Thirty or more data pairs were used for comparison.

PM2.5 sampler comparison

The comparison of RAAS PM2.5 FRM to continuous PM2.5 shown in Table 4 indicates excellent inter and intra sampler agreement for the PM2.5 samplers.

Regression analysis of the collocated RAAS yielded a slope of 0.98, correlation of 1.0, and an intercept of -0.57 showing very good agreement between pairs. Similarly the collocated And-BAM (slope 0.98, correlation 0.98, and intercept 0.69), the Met-BAM (slope 0.98, correlation 1.0, and intercept -1.19), the FDMS (slope 1.04, correlation 0.99, and intercept, 0.88), and the CAMM (slope 0.97, correlation 0.91, and intercept 2.32) (Table 4) agree well with each other. When calculated using equations 1 and 2, the RAAS has precision value of 4% (Table 3).

Table 4. PM2.5 samplers comparison

X	Y	Intercept	slope	r[1]	# samples
Precision					
RAAS[2]	RAAS	-0.57	0.98	1.0	33
And-BAM[3]	And-BAM	0.69	0.98	0.98	99
Met-BAM[4]	Met BAM	-1.19	0.98	1.0	105
FDMS[5]	FDMS	0.88	1.04	0.99	55
CAMM[6]	CAMM	2.32	0.97	0.91	96
Accuracy					
RAAS	And-BAM	-1.32	1.02	0.98	102
RAAS	Met-BAM	-1.58	1.03	1.0	102
RAAS	FDMS	3.73	1.01	0.99	102
RASS	CAMM	9.79	0.68	0.87	93

[1] r = correlation
[2] RAAS = Reference Ambient Air Monitor is a Federal reference method for PM2.5
[3] And- BAM = Thermo Andersen BAM model FH 62 C14 manufactured by Thermo Andersen Inc.
[4] Met BAM = Met One BAM model 1020 manufactured by Met One Instruments, Inc.
[5] FDMS = Filter Dynamic Measurement Systems, series 8500 manufactured by Rupprecht and Patashnick Co.
[6] CAMM = Continuous Ambient Mass Monitor manufactured by the Thermo Andersen Inc.

Continuous Samplers

The accuracy of a PM2.5 continuous sampler was determined by comparing 24-hr average data with the RAAS PM2.5 FRM (Table 4). The values of the slopes (1.02, 1.03, and 1.01 respectively), correlation (0.98, 1.0, and 0.99 respectively), and intercepts (-1.32, -1.58, and 3.73 respectively) indicate good accuracy for the And-BAM, the Met-BAM, and the FDMS respectively. For CAMM, slope of 0.68, correlation of 0.87, and intercept of 9.79 indicate poor agreement with the FRM.

Criteria for Acceptability as California Approved Samplers

The criteria used by the U.S.EPA for determining acceptability of PM10 equivalent samplers, seen below as PM10 Class II, were adopted by staff as the criteria for selecting California Approved Samplers. The criteria have been used successfully by the U.S EPA to approve a large number of samplers that are used throughout the country. We find the criteria suitable provided the tests are conducted in California and under conditions typical of areas with large populations and with persistent PM problems.

The U.S. EPA promulgated more stringent criteria in the PM2.5 regulations for PM2.5 equivalency. The new levels have been seen as quite stringent, to the point that the PM2.5 reference sampler, when compared to itself, often fails the test. They have been characterized as unnecessarily stringent, particularly in light of the increased number of data values available from continuous instruments. That feature is discussed below. It is interesting to note, however, that all samplers in the California Approved Sampler Study, except one, would have passed the more stringent PM2.5 criteria. The one that did not pass, failed only slightly with a slightly elevated y-intercept.

The U.S. EPA is developing other techniques for inter-sampler comparisons that are designed to take full advantage of the power of the increased sampling frequency of continuous samplers versus the intermittent schedule of filter based measurements. The EPA has found that the increased sampling frequency from continuous samplers would allow them to relax the nominal level of the acceptance criteria without lessening the effectiveness of the current comparative test.

Staff are following the evolving developments being discussed by the U.S.EPA , however, have selected a more stringent criteria for the California Approved Sampler at this time. The criteria have a history of being accepted by the measurement community and reliable if sampling conditions are regulated.

Table 5. Criteria for PM10 and PM2.5 (40CFR 53 Table C-1)

	PM10 Class II	PM2.5 Class II
Precision of replicate reference	5 $\mu g/m^3$ or 7%	2 $\mu g/m^3$ or 5%
Slope	1 ± 0.1	1 ± 0.05
Intercept ($\mu g/m^3$)	0 ± 5	0 ± 1
Correlation (r)	≥ 0.97	≥ 0.97

Conclusions

The staff proposes to use the accuracy and precision criteria stated in federal regulation as the U.S. EPA PM10 class II test specifications as the State's criteria for determining acceptability of a California Acceptable Sampler for PM10 and PM2.5.

For both PM2.5 and PM10, three of the four samplers evaluated in the study--the Thermo Andersen BAM (model FH 62 C14), the Met One BAM (model 1020), and the R&P FDMS (series 8500) satisfy the criteria. Consequently, staff recommends that these samplers be approved for use to measure PM mass for determining compliance with the existing and proposed State AAQS.